A method to manufacture cell-cans

Patent number: EP0732758
Publication date: 1996-09-18
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Classification:
- international: *H01M2/02; H01M2/10;* H01M2/02; H01M2/10; (IPC1-7): H01M2/02
- european:
Application number: EP19960301753 19960314
Priority number(s): JP19950055447 19950315; JP19950058579 19950317

Also published as:
US5787752 (A1)

Cited documents:
EP0629009
JP5089861
JP5021044

View INPADOC patent family

Abstract of **EP0732758**

This invention relates to a method to manufacture cell-cans by DI can method, by manufacturing a bottomed cylindrical cup-shaped intermediate product from a sheet material of which both surfaces are nickel plated and annealed in an atmosphere of inert gas making the metal nickel layer thickness and the hardness at predetermined values, then ironing the intermediate product at a predetermined ironing rate,

securing a thickness of the metal nickel layer of more than 1.0 mu m and a Vickers hardness of more than HV 200 on the side wall of finished cell-cans. By this, conventional defect problems due to the cracks generated on the intermeiate product can be sovled completely and the problem of hair-lines formed on the surface of finished cell-can can be eliminated.

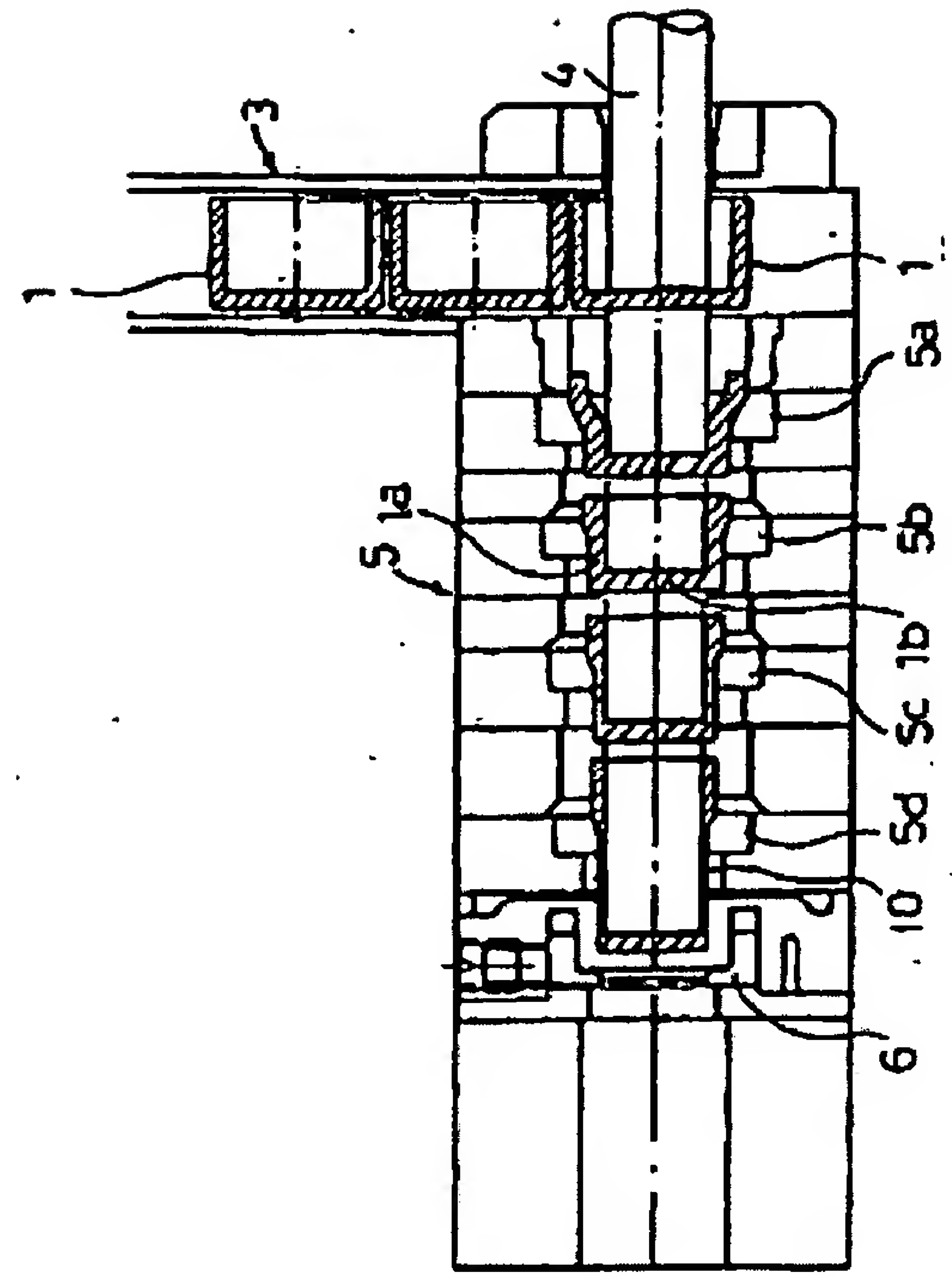

Fig. 2

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 732 758 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
18.09.1996 Bulletin 1996/38

(51) Int Cl.[6]: **H01M 2/02**

(21) Application number: **96301753.8**

(22) Date of filing: **14.03.1996**

(84) Designated Contracting States:
BE DE GB

(30) Priority: **15.03.1995 JP 55447/95**
17.03.1995 JP 58579/95

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(54) **A method to manufacture cell-cans**

(57) This invention relates to a method to manufacture cell-cans by DI can method, by manufacturing a bottomed cylindrical cup-shaped intermediate product from a sheet material of which both surfaces are nickel plated and annealed in an atmosphere of inert gas making the metal nickel layer thickness and the hardness at predetermined values, then ironing the intermediate product at a predetermined ironing rate, securing a thickness of the metal nickel layer of more than 1.0 μm and a Vickers hardness of more than HV 200 on the side wall of finished cell-cans. By this, conventional defect problems due to the cracks generated on the intermeiate product can be sovled completely and the problem of hair-lines formed on the surface of finished cell-can can be eliminated.

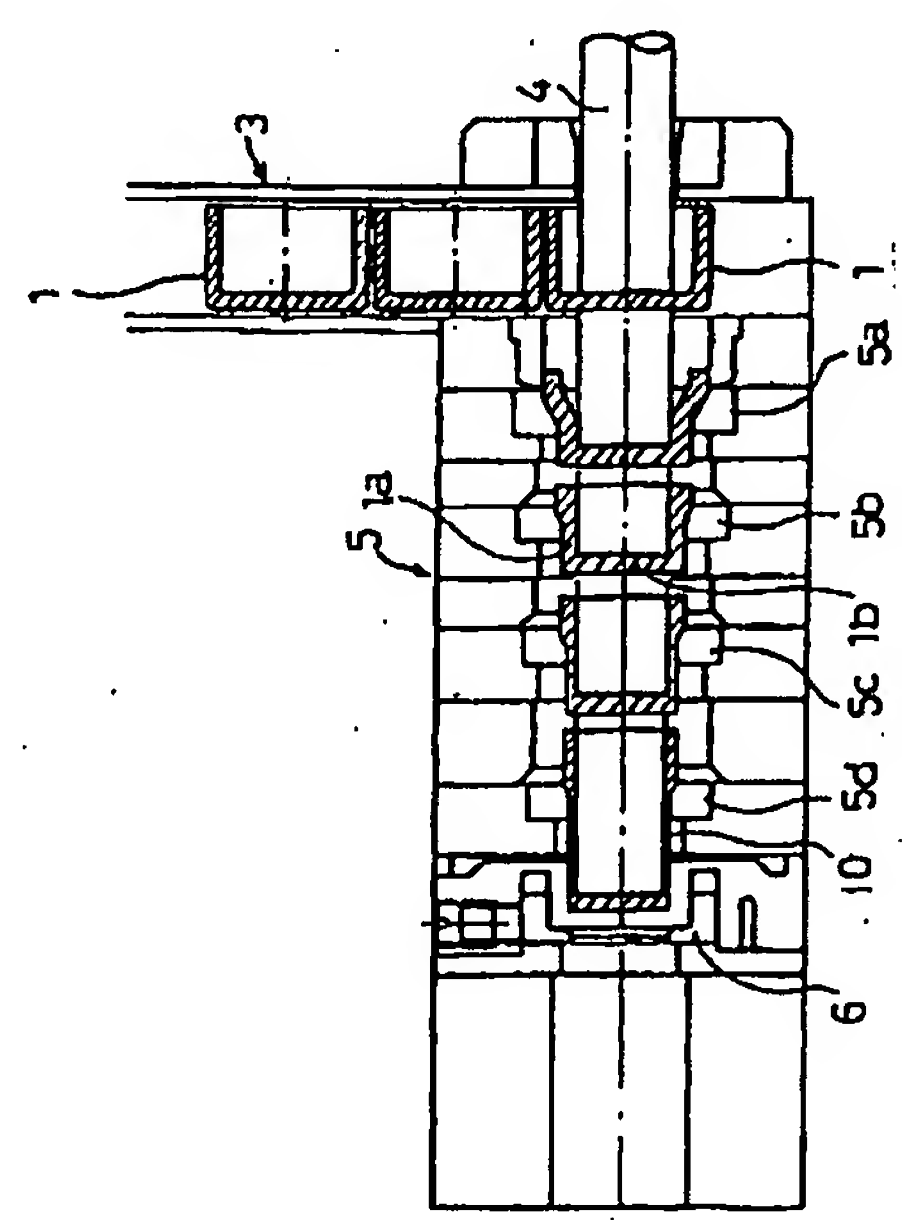

Fig. 2

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Description

BACKGROUND OF THE INVENTION

This invention relates to a method to manufacture cell-cans made of nickel-plated steel sheet accomodating cylindrical cells designed for various battery systems, and relates particularly to a method forming said cell-cans to have a thickness of sidewall thinner than that of its bottom wall.

In various battery systems typified by alkaline batteries of alkaline-manganese system, nickel-cadmium system, nickel-metal hydride system or such, and typified by lithium primary batteries employing manganese dioxide, graphite fluoride, or iron disulfide as the cathode active material and typified further by lithium secondary batteries for example lithium-ion batteries, various cells having cylindrical, rectangular, or flat shape have been developed and utilized.

Among these, a numerous types of these cells having a circular cross-section such as the button type, coin type, or cylindrical type cells made of high precision components have been developed and mass-produced because of the easiness of cell assembling works and high reliabilities of sealing of liquid or gas.

Among these, the cylindrical type cell such as the sealed secondary battery having an overall height larger than its outer diameter have been considered suitable for constructing the cells having a relatively high discharge capacity utilizing its higher mechanical strength including the high pressure strength against the increased internal gas pressure.

The method forming said cell-cans accomodating the cell elements including the positive and negative electrodes, electrolyte, separator, etc., is a kind of plastic working, and a deep drawing press method forming the cell-cans made of metal sheet such as steel sheet in several steps by using a transfer-machine consisting mainly of several compression type die-mounted press-hammers, and a spinning method by which the sheet material is drawn by rolls together with the dies and tools had been well known as typical methods. While the cell-cans manufactured by either of these methods are formed conventionally to have an equal thickness of both the bottom and the side walls, the deep drawing press method is more advantageous for the mass-production, and the cans are nickel plated in general after the forming.

In manufacturing conventional cell-cans having a nearly equal thickness of the side wall and the bottom wall, a higher mechanical strength has to be provided by employing a thicker steel sheet in proportion to the larger outside diameter of cell-can. However, in accomodating a cylindrical cell into a cell-can, the cylindrical cell-can having a circular cross-section and a relatively flat cover or bottom wall is considered structurally advantageous even if a relatively thin side wall is employed.

Since the cylindrical cell used as a power supply of portable equipment has to be made to have a lighter weight and higher discharge capacity consistently, a cell-can manufacturing method obtaining a higher internal volume by employing a larger inside diameter and a lighter weight by employing a side wall thickness thinner than the bottom wall has been developed. For example, these had been manufactured by either the DI can (drawn and ironed can) methods disclosed by the Japanese Patent Application Open-Laying Nos. Sho-18005 and Hei 5-89861.

According to these manufacturing methods, a disk sheet having a Vickers hardness of approximately HV 100 - 120 punched out of nickel plated and annealed steel sheet in an inert gas atmosphere is deep drawn by using a press machine obtaining a bottomed cylindrical cug-shaped intermediate product having a cross-section shown in Fig. 1 wherein thickness P_1 of side wall 1a and thickness Q_1 of bottom wall 1b of the intermediate product shown in Fig. 1 are nearly equal.

Then, by using a drawing and ironing machine shown in Fig. 2 performing the redrawing and ironing processes simultaneously, thickness P_1 of side wall 1a of intermediate product 1 is reduced forming a higher side wall of finished cell-can utilizing the reduced thickness P_1 of side wall 1a.

Fig. 2 shows a cross-sectional view of a typical drawing and ironing machine employed in the invented process, and a schematic working process of intermediate product 1. In Fig. 2, intermediate product 1 is intermittently placed into the individual forming positions of machine by carrier 3 where the intermediate product 1 is drawn into the outer shape of punch 4 by means of pressing punch 4 and redrawing die 5a. Although the outer diameter of intermediate product 1 is reduced considerably changing the shape of intermediate product 1 into a shape of long torso, but very little changes of the thicknesses of bottom and the side walls are produced by this redrawing process.

Then, intermediate product 1 is pressed by punch 4 and is successively passed through the first, second, and third ironing dies 5b, 5c and 5d at one motion during which thickness P_1 of side wall 1a is reduced and the height of side wall is increased in proportion to the decrease of thickness P_1, increasing the hardness of side wall somewhat during this period.

As redrawing die 5a and ironing dies 5b, 5c and 5d of the first, second, and third stages tandemly disposed in a form of concentric circle are aligned with punch 4, and the inner diameters of ironing dies 5b, 5c, and 5d are smaller in proportion to the increased number of stages. Thus, thickness P_1 of side wall 1a becomes thinner and the height of side wall becomes higher in proportion to the increaed processes of redrawing and ironing during which intermediate product 1 is passed through the multi-stage dies explained in above.

Finished product 10 went through the redrawing and multi-stage ironing processes is removed by stopper 6, and

the excess top open-end is cut-off yielding finished cell-can 2 shown in Fig. 3.

Fig. 3 shows a cross-sectional view of cell-can 2 finished by the invented method. In Fig. 3, the thicknesses of side wall 2a and bottom wall 2b are shown by P_2 and Q_2 respectively. Notice that thickness P_2 of side wall 2a of cell-can 2 is reduced to a thickness less than thickness P_2 of side wall 1a in proportion to the increased ironing stage, thickness Q_2 of bottom wall 2b is unchanged remaining thickness Q_1 of bottom wall 1b of intermediate product 1.

Comparing the new DI method over the conventional press method, a substantial reduction of the number of processes over those of conventional press method is obvious. Therefore, not only a higher productivity and a lower cost, but, at the same time, a cell-can having a lighter weight and higher discharge capacity can be obtained. Beside these, obtaining a number of advantages such as the higher mechanical strength of cell-can reducing the proba-bilities of gas and electrolyte leakage caused by the stress corrosion cracking of can, a wider application field of the DI method is now obtained.

However, fine vertical hair-lines had been observed often on the outer surface of side wall of the cell-can manufactured by the DI can method. Since the nickel plating of those cell-cans is peeled off and the surface of such hair lines is rusted easily producing poor appearances of cell-cans so that the cans of such had to be rejected. Once this kind of hair-line rejects took place, this tended to be continuously appeared on all of the cans so that all of the cans had to be rejected. These hair-lines were observed often with the high torso cell-cans such as the cans for AA (R6) size and AAA (R03) size cell-cans manufactured by applying a high ironing rate at the redrawing and ironing process.

Whereas the bottomed cylindrical cup-shaped intermediate product 1 having a higher overall height against the outer diameter had to be prepared in manufacturing the cells having a dimen-sional ratio of the outer diameter to the overall height exceeding 3.5, the hair-line troubles were often produced at a high rate within these intermediate product stages.

The present invention relates mainly to a method to manufacture the cell-cans solving these problems. First of all, the possible causes of these troubles were analyzed and determined by conducting below-shown series of experiments. In there, the both surfaces of 0.4 mm thick hoop-formed steel sheet are nickel electrolytic plated for a thickness of 3.5 μm, and this is annealed at a temperature of 600°C for a period of 50 hrs in an atmosphere of nitogen gas. Fig. 4 shows a schematic metallugical microscopic observation made on a cross-section of annealed sheet material.

Fig. 4 shows clearly 3.5 μm-thick nickel layer 6 formed on the surface of steel sheet 11 is separated into metal nickel layer 12 having a thickness p_0 of 2.2 μm and nickel-iron alloy layer 13 having a thickness q_0 of 1.7 μm respectively makig a total thickness of 3.9 μm. The nickel-iron alloy layer 13 is formed by the thermal diffusion of nickel from the nickel plated layer into steel sheet 11 yielding metal nickel layer 12 having a thickness reduced by 1.3 μm counting from the beginning.

While the metal nickel layer 12 having a low hardness and a high drawing rate acting as a lubricant at the redrawing and ironing, the hardness of nickel-iron alloy layer 13 is higher. Thus, if steel sheet 11, metal nickel layer 12 and nickel-iron alloy layer 13 are ironed reducing the respective thicknesses according to the respective ironing rates of these, there should be no troubles.

Whereas the ironing process of metal nickel layer 12 had been controlled conventionally to secure a thickness of 0.64 ~ 0.96 μm, it have been found that the surface of metal nickel layer 12 is often broken by nickel-iron alloy layer 13 having a high hardness, and a part of nickel-iron alloy layer 13 is exposed out of the surface of metal nickel layer 12 causing a direct contact of the nickel-iron alloy on the ironing dies, a partial damage thereof leaving hair-line scratches on the outer surface of side wall of cell-can.

Studying the thorough conditions between the thickness of nickel plated layer and the annealing, the relationship between the hardness and the thickness of metal nickel layer formed on the annealed steel sheet and the ironing rates at the drawing and ironing process have been determined. By these, a new cell-can manufacturing method reducing the probability of reject problems such as the cracks of bottomed cylindrical cup-shaped intermediate products is obtained, accomplishing higher industrial effects such as a higher manufacturing yield, lower production cost, and higher reliability of cell-cans.

SUMMARY OF THE INVENTION

The first objective of this invention is to prevent the rejects due to the hair-lines produced on the cell-cans. That is, a method to solve the hair-line problems completely by manufacturing the cell-cans from the sheet material of which both surfaces are nickel plated and annealed in an atmosphere of inert gas, by preparing a bottomed cylindrical cup-shaped intermediate product by applying a deep drawing to the sheet material securing a thick-ness of metal nickel layer of more than 1.0 μm by applying an ironing work on the side wall of said intermediate product reducing the wall thickness and increasing the height of side wall securing a thickness of metal nickel layer of "a" μm of both metal nickel layers remaining on the surfaces of annealed steel sheet in proportion to the ironing rate "b" % accomplished at the ironing work satisfying a below-shown relationship of:

$$\text{"a" } \mu m \times (100 - \text{"b"})/100 \geq 1.0 \ \mu m.$$

The second objective of the invention is to prevent the crack rejects in manufacturing the bottomed cylindrical cup-shaped intermediate products formed into long torso cells. That is, the second objective of the invention is to offer a method to prevent the crack rejects in manufacturing the bottomed cylindrical cup-shaped intermediate products by applying a deep drawing onto the nickel-plated steel sheet annealed in a nitrogen atmosphere to have a Vickers hardness of HV 80 ~ 90, and to form these into cell-cans by ironing the side wall of the bottomed cylindrical cup-shaped intermediate product reducing its thickness increasing the height of said side wall and attaining a Vickers hardness of more than HV 200.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a cross-sectional view of bottomed cylindrical cup-shaped intermediate product of the invention.

Fig. 2 shows a cross-sectional view of the drawing and ironing machine which is used in the manufacturing method of the invention.

Fig. 3 shows a cross-sectional view of finished cell-cans to be formed into a long torso cells manufactured by the invented method.

Fig. 4 shows a schematic metallurgical microscopic photograph taken on a cross-section of the one side surface of steel sheet of which both surfaces are nickel plated and annealed thereafter.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Embodiment-1

After the both surfaces of 0.4 mm thick hoop shaped steel sheet are nickel plated attaining various nickel thicknesses by an electrolytic plating, the steel sheet is annealed in an nitrogen atmosphere varying its temperature and period in order prepare samples. The cross-sections of each samples are observed by a metallurgical microscope determining the thicknesses of metal nickel layer and nickel-iron ally layer. After this, bottomed cylindrical cup-shaped intermediate products such as shown in Fig. 1 are formed from a disk punched out of steel sheet by applying a deep drawing process. Then, after applying an ironing process to the intermediate product by using a drawing and ironing machine shown in Fig. 2 in order to attain a predetermined ironing rate, the finished cell-can is obtained by cutting off the excess end of top opening. The result of these processes is summarized and shown in Table 1.

The thicknesses of all of the metal nickel layers secured on the both surfaces of side walls of finished cell-cans of Sample Nos. 1, 2 and 3 shown in Table 1 are more than 1.0 μm, and no conventional hair-line defects were observed on the outer surface of side wall of finished cell-cans at these conditions.

Table 1

Sample Number	1	2	3
Thickness of nickel plated layer (μm)	3.5	3.5	5.0
Annealing condition			
Temperature (°C)	600	600	650
Period (hr)	50	24	50
Thickness of metal nickel layer on the sheet material (μm)	2.2	3.2	3.1
Thickness of the nickel-iron alloy layer (μm)	1.7	0.5	-
Total thickness of side wall of intermediate product (mm)	0.40	0.40	0.40
Ironing rate (%)	50	55	60
Finished cell-can			
Thickness of side wall (mm)	0.20	0.18	0.16
Total thickness of metal nickel layer of side wall (μm)	1.1	1.4	1.2

By specifying the thickness of metal nickel layer existing on the both surfaces of sheet material which the intermediate products are produced by "a" μm (corresponding to p_0 shown in Fig. 4,) and the ironing rate in drawing and ironing processes as "b" %, Relation (1) shown below is established.

$$"a"\ \mu m \times (100 - "b")/100 \geq 1.0\ \mu m \quad (1)$$

Relation (1) can be rewritten in a form (2) shown below.

$$"a"\ \mu m \geq 1.0\ \mu m \times 100/(100 - b) \quad (2)$$

Once the ironing rate "b" % were established from Relations (1) and (2), the thickness "a" µm of metal nickel layer existing on the both surfaces of annealed steel sheet material can be determined. The thickness "a" µm of metal nickel layer can be set at an arbitral value by varying the thickness of the first nickel plating and the annealing condition.

Moreover, while the thicknesses of metal nickel layers existing on the both surfaces of the side wall of cell-cans is an important factor preventing the hair-lines on the outer surface of side wall of cell-cans in employing a DI can method, the formation of nickel-iron alloy layer between the steel sheet and the nickel plated layer produced by the nickel diffusion effect during the multi-stage ironing with redrawing and ironing process is an essential and important condition in respect of the prevention of peeling of metal nickel layer during the multistage ironing processes.

(Embodiment-2)

In here, bottomed cylindrical cup-shaped intermediate products such as shown in Fig. 1 having an outer diameter of 16.5 mm and an overall height of 20.44 mm are prepared by applying a deep drawing produced by a press machine. The respective thicknesses P_1 and Q_1 of side wall 1a and bottom wall 1b of the immediate product are the same with that of the sheet material which is 0.25mm.

Then, after applying successive ironing processes attaining an ironing rate of 32 % to the intermediate product by using a machine shown in Fig. 2, the excess end formed at the top opening is cut-off and removed obtaining an AAA size cell-can shown in Fig. 3. The outer diameter, the overall height, and thickness P_2 of side wall 2a of the finished cell-can are 9.98 mm, 43.50 mm and 0.17 mm respectively.

Although these thicknesses are less than the thickness of starting sheet material, thickness Q_2 of bottom wall 2b remains same as the initial thickness which is 0.25 mm. Moreover, the Vickers hardness of side wall of finished cell-can is found being increased to a value of HV 202. The Vickers hardnesses of side wall of finished cell-cans obtained by varying the ironing rate are tabulated in Table 2 showing a tendency of higher hardness of finished side wall in proportion to the higher ironing rate. Then, the mechanical strengths of cell-cans are evaluated by determining the loads producing cell-can cracks by expansion and the tensile strengths of cell-can itself.

Table 2

Sample No	Ironing Rate	Thickness	Vickers Hardness
11	25 %	0.188 mm	HV 195
12	32 %	0.170 mm	HV 202
13	35 %	0.163 mm	HV 205
14	45 %	0.138 mm	HV 215

The result of these shows that the mechanical strengths of cell-cans of sample Nos. 12 ~ 14 excluding the cell-can of sample No. 11 are satisfactory for the practical use attaining side wall Vickers hardnesses of more than HV 200. Moreover, these facts have been confirmed also by repeating this experiment, telling that the adequate cell-can mechanical strength yielding a side wall Vickers hardness of more than HV 200 can be obtained when an ironing rate of more than 30 % is employed. In this case, a steel sheet material having a Vickers hardness of approximately HV 85 which is same as that of starting material employed in this case has been employed.

Although cases employing the sheet material having a Vickers hardness of HV 85 have been explained, the prevention of crack defects in manufacturing the bottomed cylindrical cup-shaped intermediate products to manufacture cell-cans having a height/outer-diameter ratio of more than 3.5 can be accomplished by employing a nickel-plated steel sheet showing a Vickers hardness within a range of HV 80 ~ 90 after annealing. However, in order to produce cell-cans with side wall having a Vickers hardness of more than HV 200, the ironing rate has to be set a value higher than the case employing Vickers hardness of HV 85 in cases employing a steel sheet material having a Vickers hardness of HV 80, and the ironing rate may be set at a lower value in a case steel sheet having a Vickers hardness of HV 90 is employed.

As above described detailed explanations, by manufacturing a bottomed cylindrical cup-shaped intermediate product from the sheet material of which both surfaces are nickel plated and annealed in an atmosphere of inert gas making the metal nickel layer thickness and the hardness at predetermined value, and then ironing the intermediate product at a predetermined ironing rate, the chances of rejects due to the crack defects produced on the bottomed cylindrical

cup-shaped intermediate product and rejects due to hair-lines produced on the finished cell-cans can be eliminated completely.

Since the probabilities of these kinds of defects can be eliminated from cell-cans having a height/outer-diameter ratio of more than 3.5 particularly, the present invention is to offer a new method manufacturing cell-cans without defects producing a high industrial value.

Though the above-described explanations have been made consistently on the cell-cans to be formed into cylindrical cells, the application of present invention is by no means not restricted only within the method to form cylindrical cells, but is applicable to button type and coin type cells also.

Claims

1. A method to manufacture cell-cans securing metal nickel layers on both sides of side wall of cell-cans having a thickness more than 1.0 μm: comprising a process to form bottomed cylindrical cup-shaped intermediate products starting from steel sheet of which both sides are nickel-plated and annealed, a process to form these into cell-cans with an increased side wall height and a reduced side wall thickness by applying a successive ironing processes to said intermediate products.

2. A method to manufacture cell-cans according to Claim 1, wherein the thickness "a" of metal nickel layer existed on both surfaces of plated and annealed steel sheet material is specified to satisfy the below-shown relation "a" $\mu m \times (100 - \text{"b"})/100 \geq 1.0\ \mu m$ according to the ironing rate "b" of said drawing and ironing process.

3. A method to manufacture cell-cans according to Claims 1 and 2, wherein the thickness "a" of metal nickel layer existed on both surfaces of steel sheet after annealing is controlled to be more than 2.0 μm when an ironing rate of more than 50 % is applied to said drawing and ironing process.

4. A method to manufacture cell-cans according to Claims 1 and 2, wherein the Vickers hardness HV of said side wall of cell-cans manufactured by using a steel sheet material having a Vickers hardness HV in a range from 80 to 90, is adjusted to be more than 200.

5. A method to manufacture cell-cans according to Claim 1 to Claim 4, wherein the dimensional ratio of the overall height to the outer-diameter of finished cell-can is more than 3.5.

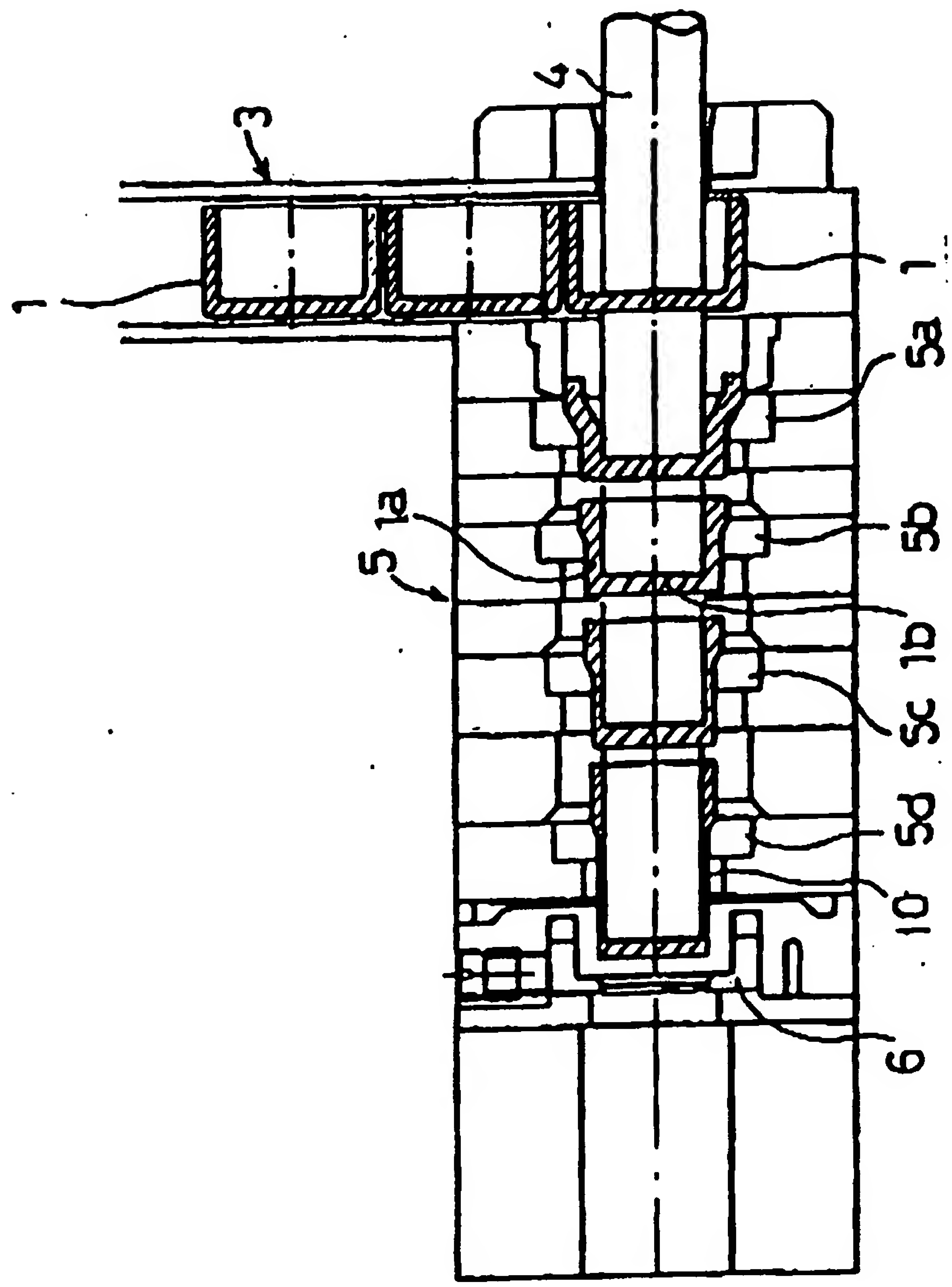

Fig. 2

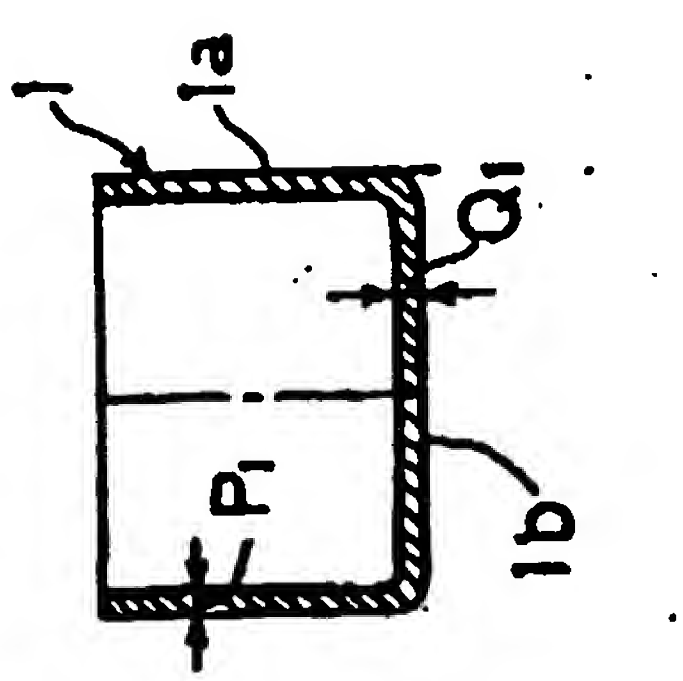

Fig. 1

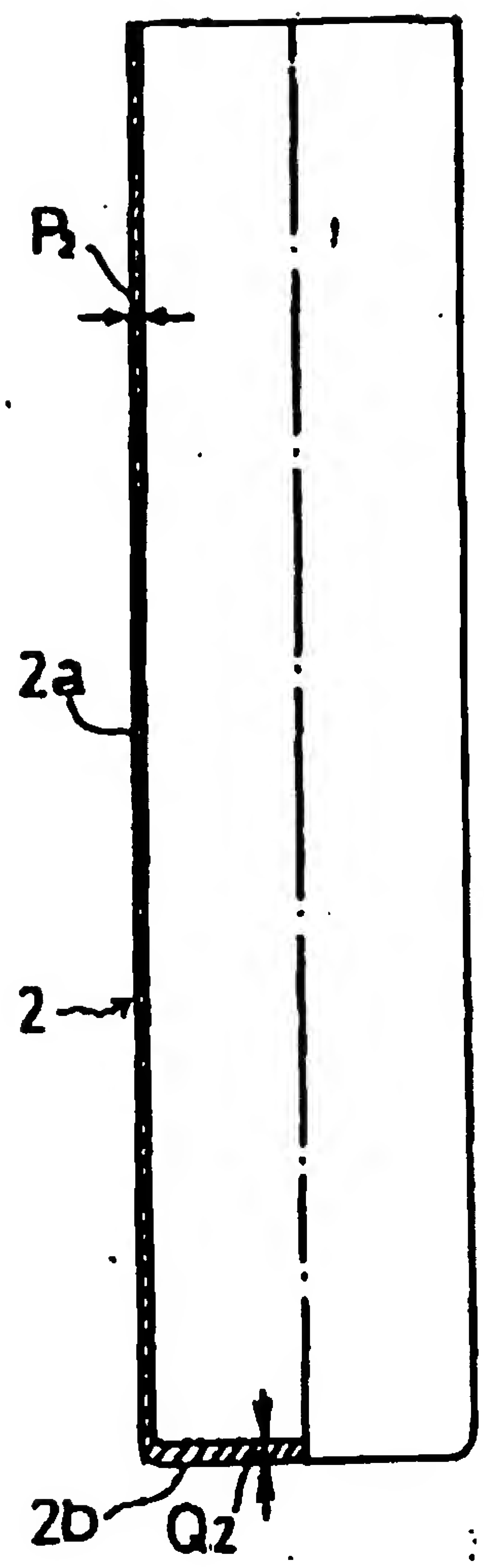

Fig. 3

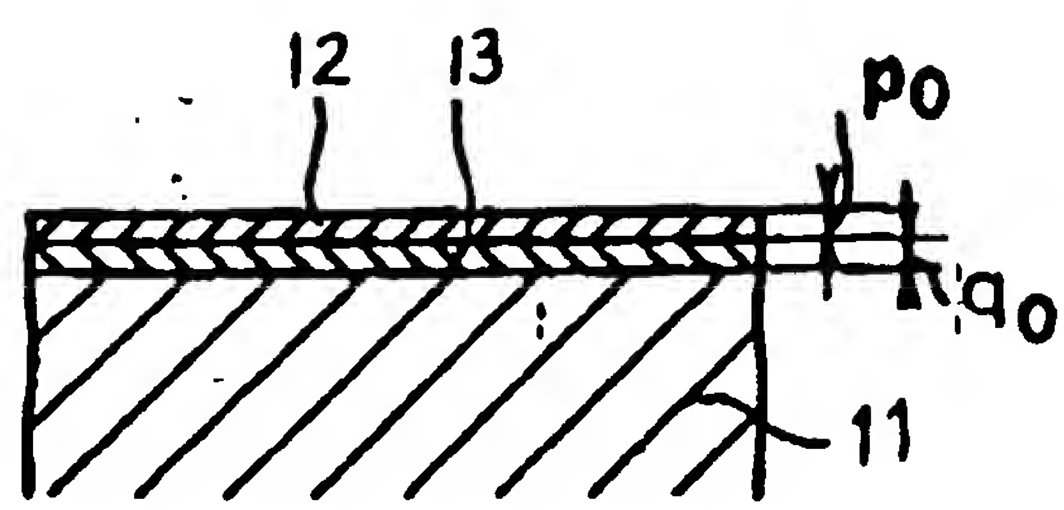

Fig. 4

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EUROPEAN SEARCH REPORT

Application Number
EP 96 30 1753

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP-A-0 629 009 (KATAYAMA TOKUSHU KOGYO KK) 14 December 1994 * page 12, line 2 - line 7; claims 1-36 * * page 6, line 12 - line 18 * ---	1	H01M2/02
D,A	PATENT ABSTRACTS OF JAPAN vol. 017, no. 424 (E-1410), 6 August 1993 & JP-A-05 089861 (MATSUSHITA ELECTRIC IND CO LTD), 9 April 1993, * abstract * ---	1-5	
A	PATENT ABSTRACTS OF JAPAN vol. 017, no. 289 (E-1375), 3 June 1993 & JP-A-05 021044 (KATAYAMA TOKUSHIYU KOUGIYOU KK), 29 January 1993, * abstract * -----	1-5	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

H01M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	11 July 1996	Battistig, M

CATEGORY OF CITED DOCUMENTS

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